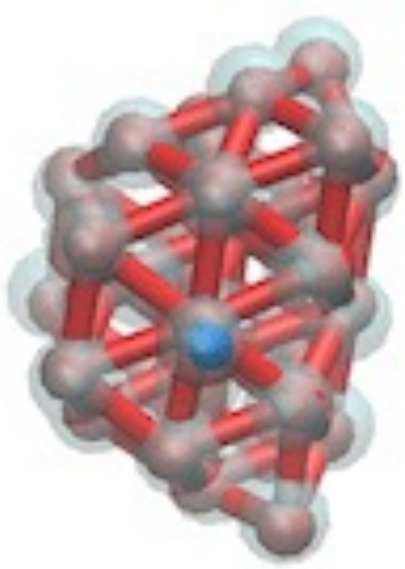
materials design

Atomistic-scale Simulations of Realistic, Complex, Reactive Materials: The ReaxFF Reactive Force Field and its Industrial and Academic Applications



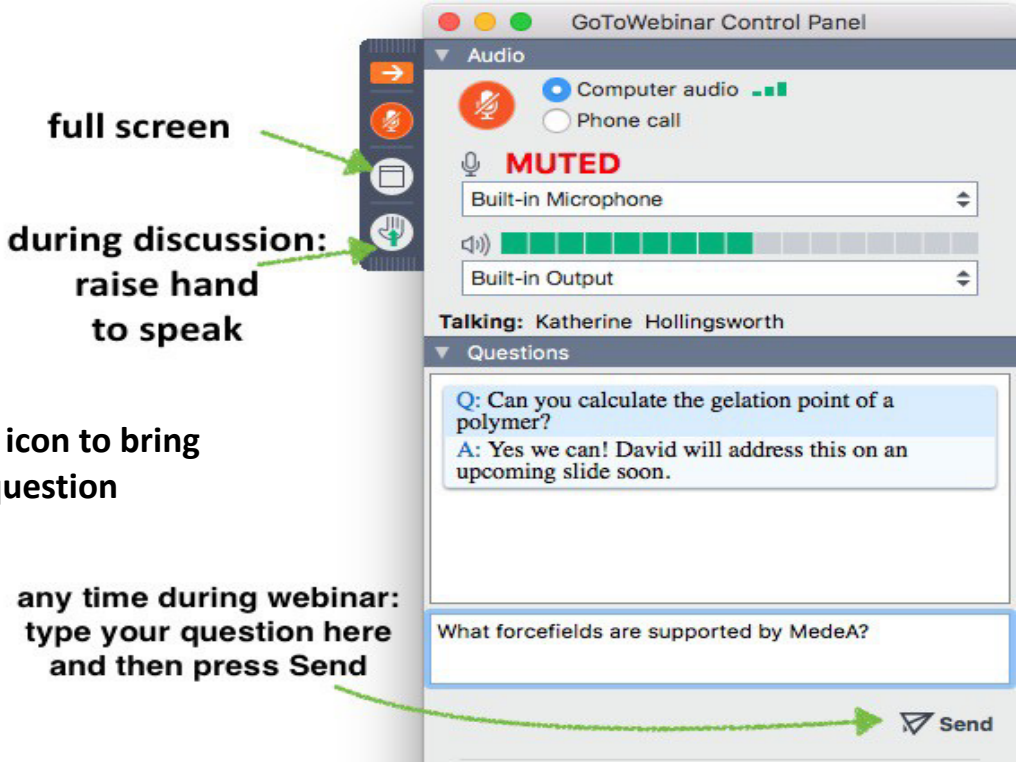
March 28-30, 2022

Materials Design Webinar Series

- Each session runs several times to accommodate schedules
  - Share the webinar series with your colleagues!
  - Registration details http://www.materialsdesign.com/webinars
- We will be recording this webinar
  - Watch any of our earlier webinars anytime
  - We will post upcoming webinars on the webinar page
- Vote for the next webinar topic!
  - Take a 2 minutes brief survey at the end of the webinar!
- Audio issues
  - Log out and log back in again
  - Check your audio output
  - Google Chrome (most recent 2 versions) Mozilla Firefox (most recent 2 versions) Apple Safari (most recent 2 versions) Microsoft Edge (most recent 2 versions)

materials design

Please Ask Questions!



Use the raise hand icon to bring attention to your question

materials design

Webinar Speakers

Katherine Hollingsworth

Dr. Ray Shan

Professor Adri van Duin

RxFF Consulting

and Pennsylvania State University

Webinar Presenter

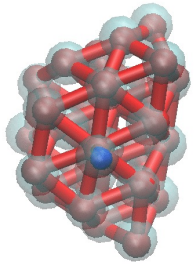
Atomistic-scale simulations of realistic, complex, reactive materials: the ReaxFF reactive force field and its industrial and academic applications

Adri van Duin
Distinguished Professor in Mechanical Engineering
with courtesy appointments in Chem.Eng, Chemistry, MatSE and Eng.Sci.Mech.
Director, Materials Computation Center
CTO, RxFF_Consulting

with contributions from
Dooman Akbarian, Dundar Yilmaz, Nadire Nayir, Mert Sengul, Margaret Kowalik, Ben Evangelisti, Kate Penrod and Jamil Hossain

Penn State University,
240 Research East Building
phone: 814-8636277
E-mail acv13@psu.edu

RxFF_Consulting
E-mail: contact@rxffconsulting.com



e-ReaxFF simulation of nitrogen migration over a Ir-cluster

Material Design
March 28, 2022

PennState

Current Penn State group members and projects

Postdoctoral staff

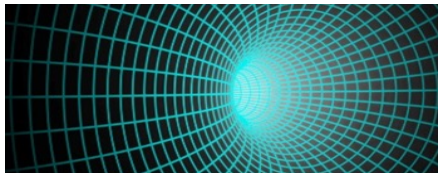
Dr. Yun-Kyung Shin	Metal alloys, Sulfur-embrittlement, Proteins, Catalysis
Dr. Nadire Nayir	2D-materials, surface catalysis
Dr. Dundar Yilmaz	Ferroelectrics, polymers
Dr. Malgorzata Kowalik	Carbon fibers, 2D-materials
Dr. Qian Mao	Carbon fibers, 2D-materials
Dr. Tao Wang	2D-materials, carbonates
Dr. Kate Penrod	Electrocatalysis
Dr. Simon Delattre (MCC)	Machine Learning

PhD-students (major)

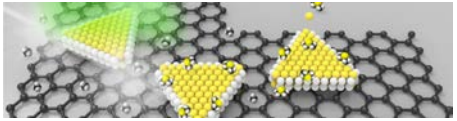
Jamil Hossain (ME)	Battery interface simulations
Nabankur Dasgupta (Eng.Sci.Mech)	Polymer hydrolysis, supercritical water, water catalysis
Siavash Rajabpour (ChemEng)	Carbon fibers, chemical vapor deposition
Karthik Ganeshan (ME)	MXene/water interfaces
Wenbo Zhu (ME)	Cu-catalysis
Yawei Gao	Additive Manufacturing
Mahdi Talkhoncheh (ChemEng)	Battery interfaces
Kamyar Roshan (Elect.Eng)	Battery interfaces
Jessica Schulze (Chem)	Water vitrification
Benjamin Evangelisti (Chem)	Redox nanomaterial growth
Alireza Sepehrinezhad	Ferroelectric materials
Mengyi Wang	2D-chalcogenice growth
GaUn Jeong	Boron nitride growth

The Material Computation Center within Material Research Institute

MCC

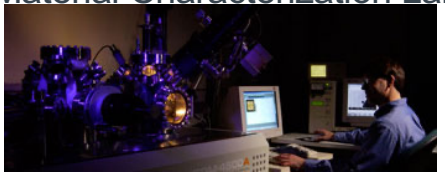


2DCC



Nanofab

Material Characterization Lab



Four Lab Solution: Theory, Synthesis, Fabrication, Characterization

Evaluate material candidates

100 possible candidates

Computational methods

Top 10 candidates

Synthesize materials

Fabricate materials

- MCC allows Nanofab/MCL/2DCC to focus on high-probability materials

Characterize materials

- Simulation is relatively inexpensive – allows testing of out-of-the-box concepts

2DCC PennState

MCC affiliated faculty – length scales


Ed O'Brien

Bladimir Ramos-Alvarado


Leonid Berlyand

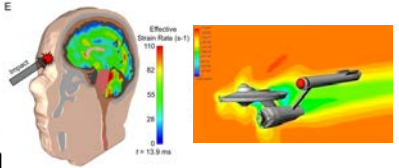
Design


Will Noid


Sulin Zhang

Multigrain


Chris Giebin




Michael Janik

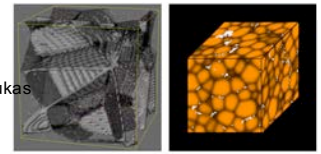
Vin Crespi


Janna Maranas


Adri van Duin

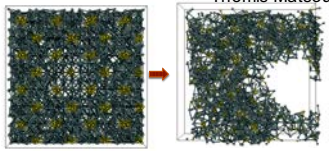
Grain/Grain boundaries


Themis Matsoukas



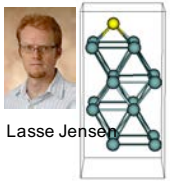

Ismaila Dabo


Jorge Sofo



Phase field, CALPHAD


Reuben Kraft


Lasse Jensen


Susan Sinnott

Empirical force fields (1-10^8 atoms)


Zi-Kui Liu


LongQing Chen


Douglas Werner


Kristen Fichthorn


John Mauro

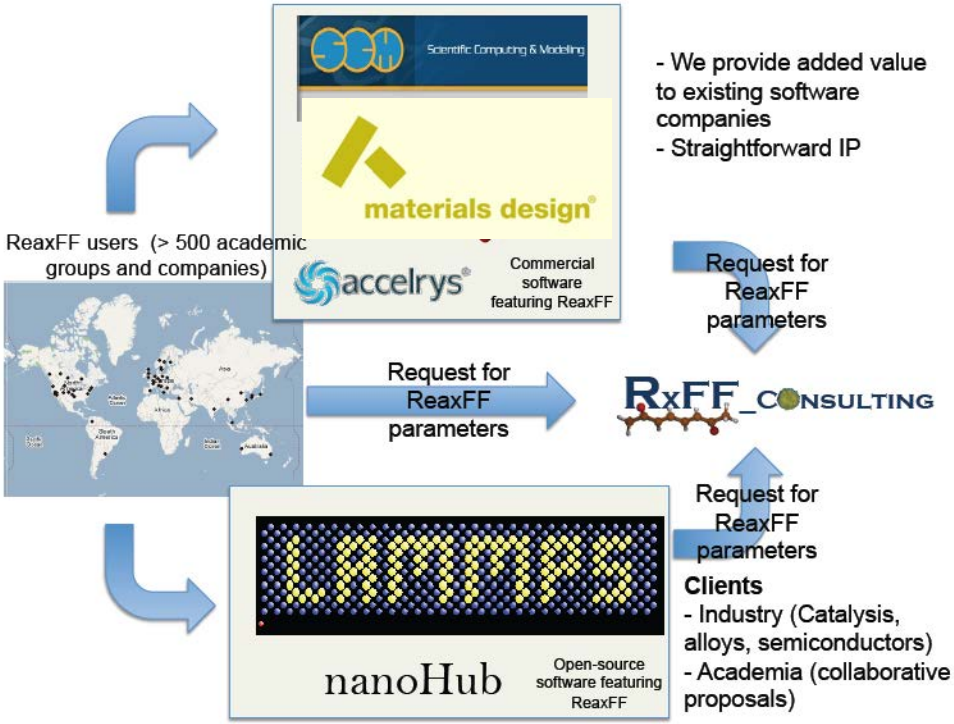

Scott Millner

Quantum mechanics (1-1000 atoms)

PennState

- Currently 20 affiliated faculty
- World-class simulation capability at all length scales – including connections between scales
- Extension with senior technical staff planned in 2020

RxFF_CONSULTING



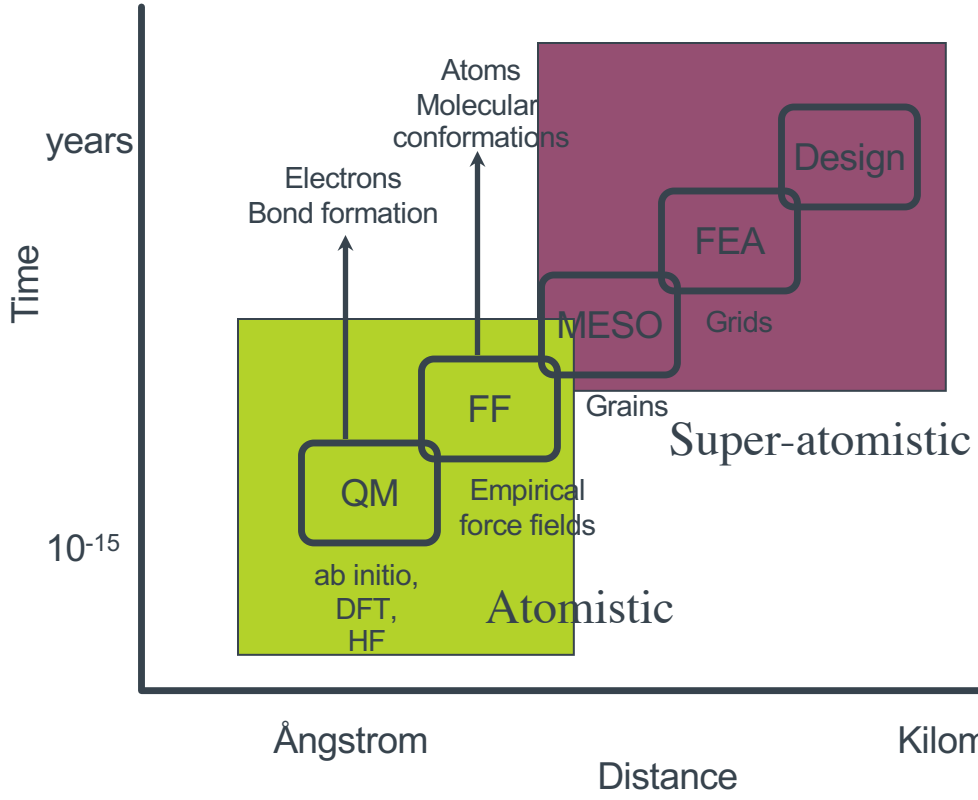
Dr. Adri van Duin
CTO

Dr. Diana van Duin
CEO

- Founded Sept. 2013
- Completed over 25 projects
- Industry, academia clients

Company website: http://www.rxffconsulting.com/
E-mail: contact@rxffconsulting.com

Simulations on the dynamics of chemical reactions



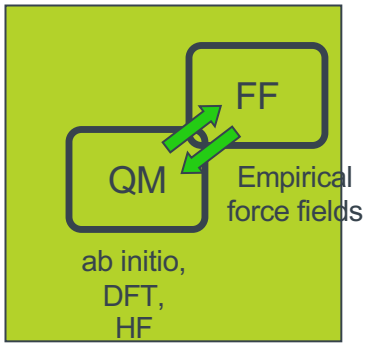
QM methods:
- Fundamental
- Expensive, only small systems

FF methods
- Empirical; need to be trained
- Much cheaper than QM, can be applied to much larger systems

materials design

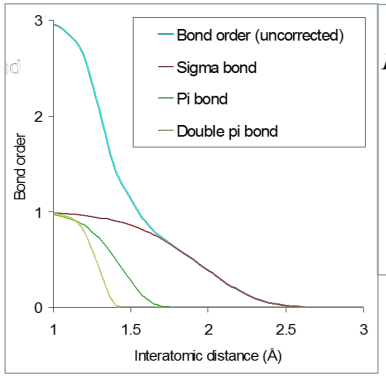
QM and FF-based approaches to reactive MD

- Option 1: Burn CPUs with QM/MD (e.g. Raty et al., PRL 2005, Wang et al. Nature Chem 2014)
- Option 2: use empirical assumptions to make QM faster (semi-empirical methods)
    - CINDO/MINDO/AM1/MOPAC (e.g. Pople and Segal, JCP 1966; Stewart, J. Comp. Chem. 1989)
    - Tight-binding (e.g. McMahan and Klepeis, PRB 1997)
    - Analytical Bond Order Potentials (e.g. Pettifor and Oleinik, PRB 1999)
- Option 3: Add ability to simulate reactions to FF-method (empirical bond-order based force fields)
    - Tersoff /Brenner /AIREBO (Tersoff, PRL 1988; Brenner, PRB 1990, Stuart et al., JCP 2000)
    - LCBOP (de Los et al., PRB 2005)
    - EDIP (e.g. Bazant and Kaxiras, PRL 1996)
    - COMB (e.g. Liang et al. JPC-A 2012)
    - MEAM (e.g. Nouranian and Baskes, PCCP 2014)
    - ReaxFF (e.g. van Duin et al. JPC-A 2001)
- Option 4: Neural Network based potentials

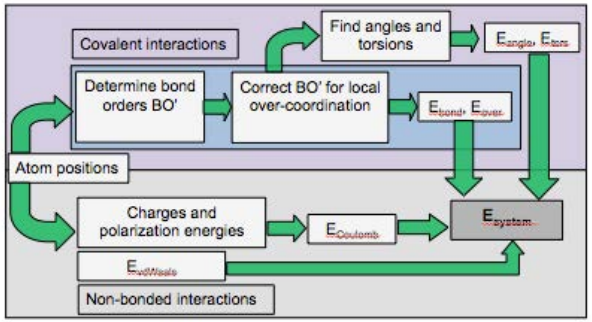


materials design

Key Features of ReaxFF

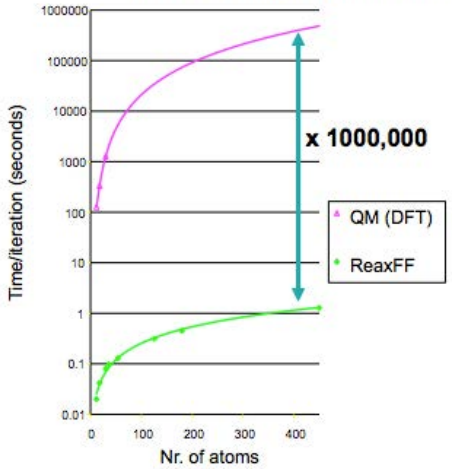


$$BO'_{ij} = \exp\left[p_{bo,1}\cdot\left(\frac{r_{ij}}{r_o^{\sigma}}\right)^{p_{bo,2}}\right] + \exp\left[p_{bo,3}\cdot\left(\frac{r_{ij}}{r_o^{\pi}}\right)^{p_{bo,4}}\right] + \exp\left[p_{bo,5}\cdot\left(\frac{r_{ij}}{r_o^{\pi\pi}}\right)^{p_{bo,6}}\right]$$



$$E_{system} = E_{bond} + E_{val} + E_{tors} + E_{vdWaals} + E_{Coulomb} + E_{over} + E_{under}$$

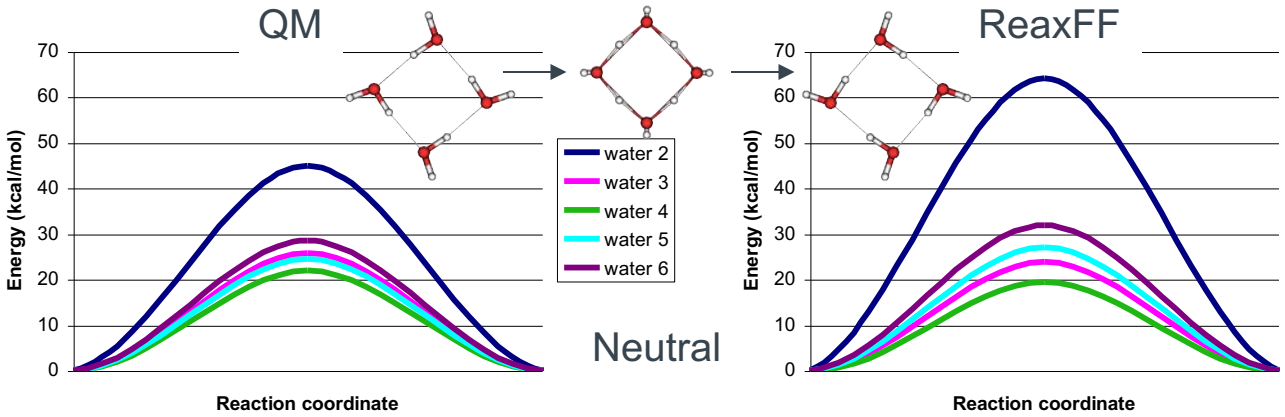
- To get a smooth transition from nonbonded to single, double and triple bonded systems ReaxFF employs a bond length/bond order relationship[1,2,3]. Bond orders are updated in every iteration
- All connectivity-dependent interactions (i.e. valence and torsion angles) are made bond-order dependent.
- Nonbonded interactions (van der Waals, Coulomb) are calculated between every atom pair
- Polarizable charges are calculated using the EEM method[4]



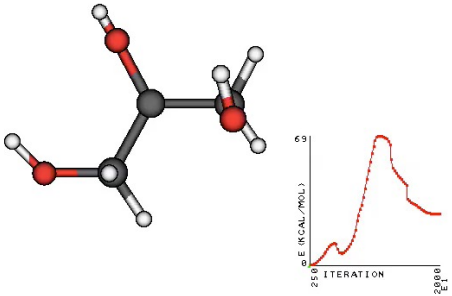
ReaxFF allows for reactive MD-simulations on systems containing more than 1000 atoms

[1]Brenner, D. W., *PRB* (1990) | [2]Tersoff, J., *PRL* (1988) | [3]Abell, G. C., *PRB* (1985) | [4]Mortier, W. J., et al. *JACS* (1986)

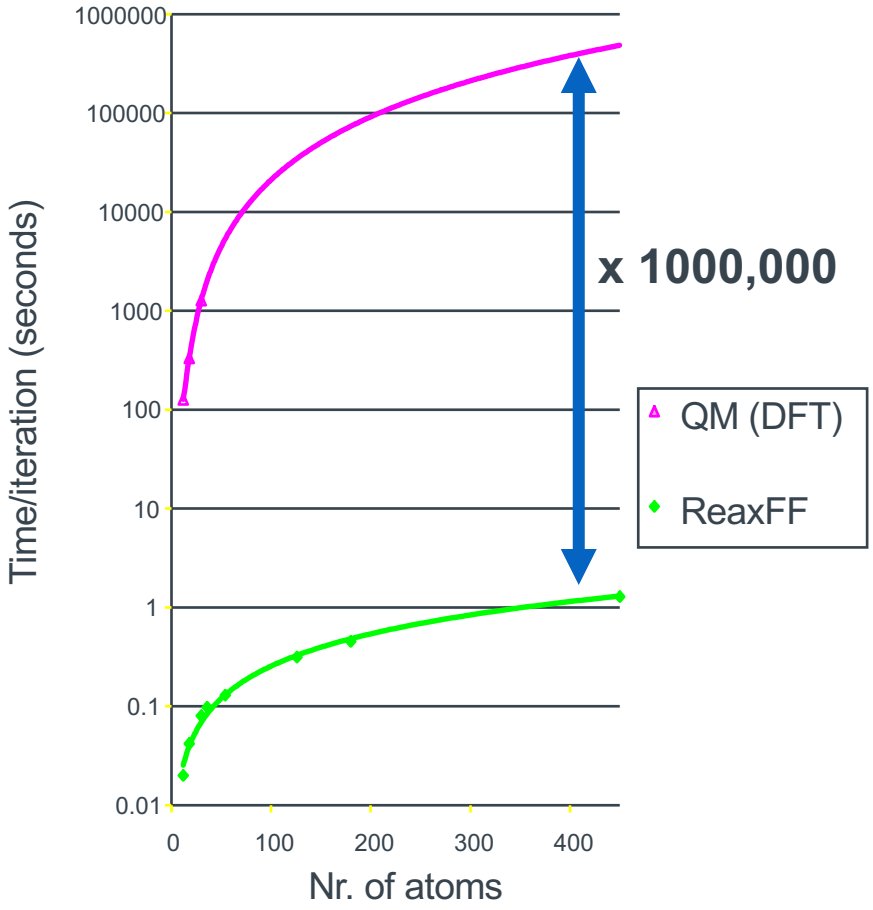
Reaction barriers for concerted reactions



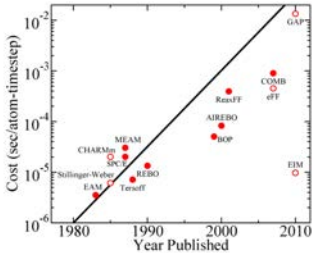
ReaxFF barrier for Grob fragmentation (collaboration with John Daily, Boulder). QM barrier: 65 kcal/mol (Nimlos et al., JPC-A 2006)



ReaxFF Computational expense



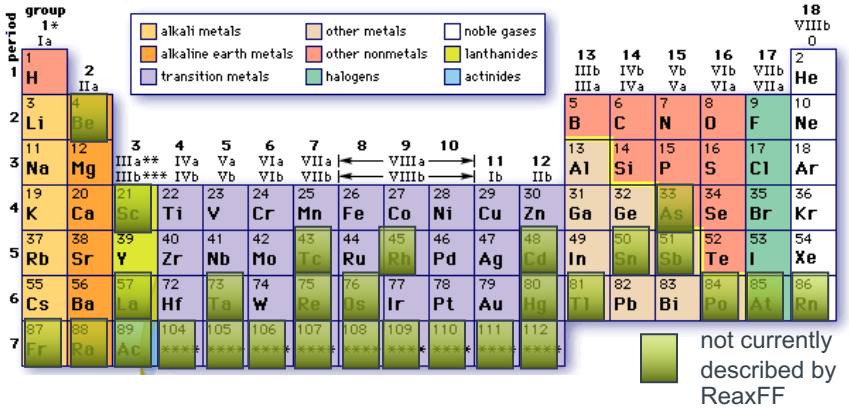
-ReaxFF allows for reactive MD-simulations on systems containing more than 1000 atoms
- ReaxFF is 10-50 times slower than non-reactive force fields
- Better scaling than QM-methods (NlogN for ReaxFF, N^3 (at best) for QM



Current development status of ReaxFF

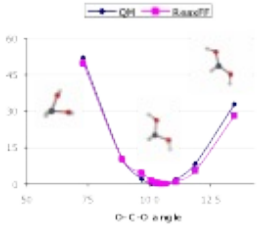
- ReaxFF combines covalent, metallic and ionic elements allowing applications all across the periodic table
- All ReaxFF descriptions use the same potential functions, enabling application to interfaces between different material types
- Code has been distributed to over 3000 research groups
- Parallel ReaxFF (LAMMPS/ReaxFF) available as open-source
- MedeA provides a user-friendly GUI supporting LAMMPS/ReaxFF

ReaxFF transferability

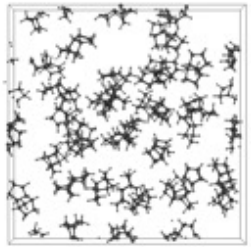


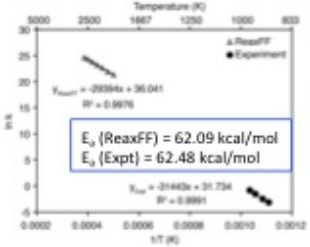
materials design

Combustion/catalysis

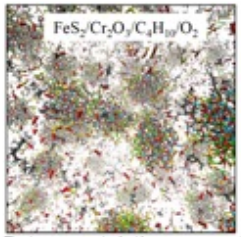


Angle distortion in $CH_2(OH)_2$
(Chenoweth et al. JPC-A 2008)

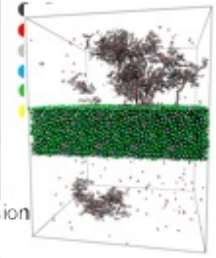




JP-10 pyrolysis – comparison with experiment
(Chenoweth et al. JPC-A 2008)

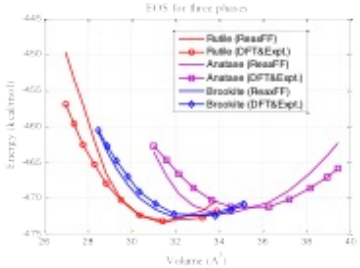


Butane catalytic conversion on pyrite/chromia
(Shin et al. ACS Catalysis 2015)

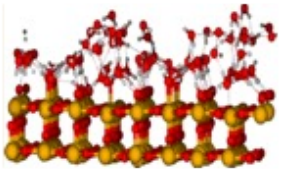


Coal combustion on a MoNi alloy surface
(Vasenkov et al. JAP 2012)

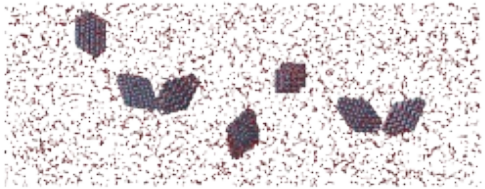
Crystal growth



TiO_2 equations of state
(Kim et al. Langmuir 2013)

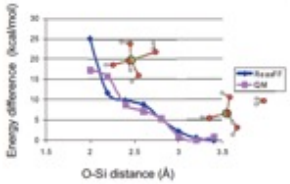


Water structure and reactivity on TiO_2-surfaces
(Raju et al. JPC-C 2013)

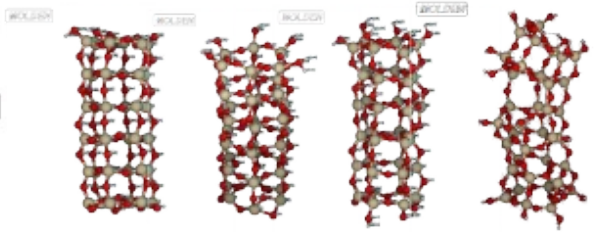


Oriented crystal growth of TiO_2 NPs in water
(Raju et al. Nano Letters 2014)

Hydrolysis reactions on mineral surfaces



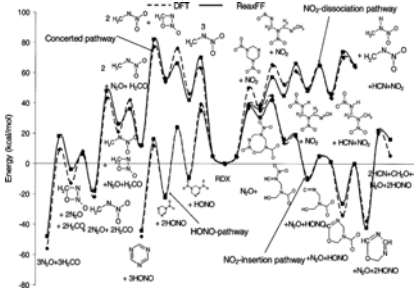
Water approach to silanol
(Fogarty et al. JCP 2010)



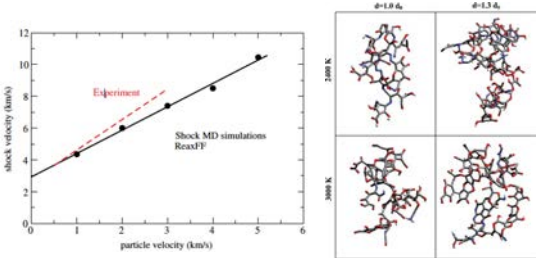
Strain-dependent hydrolysis reactions on a silica nanowire
(Yeon et al. JPC-C 2016)

Water diffusion in clay/zeolite interfaces
(Pitman et al. JACS 2012)

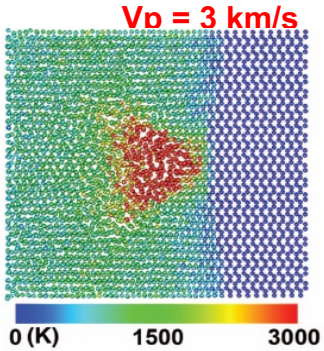
High energy materials



RDX dissociation channels (Strachan et al. JCP 2005)

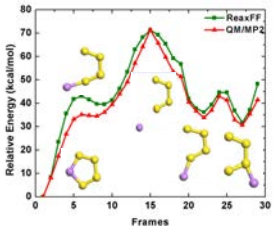


Comparison with experiment – shock velocity and carbon clustering (Strachan et al. PRL 2013; Zhang et al. JPC-A 2009)

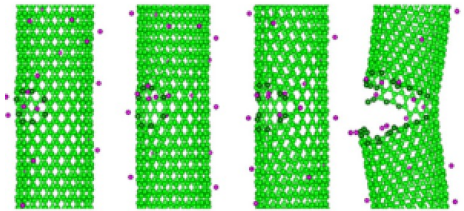


Void effects on HE-response (Nomura et al. PRL 2007)

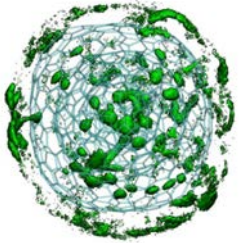
Batteries



Li-migration around S_4 (Islam et al. PCCP 2015)

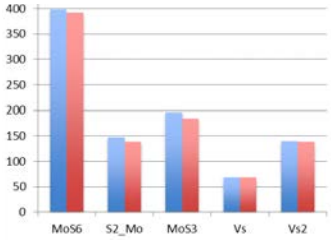


Li-etching of a defected, strained carbon nanotube (Huang et al APL 2013)

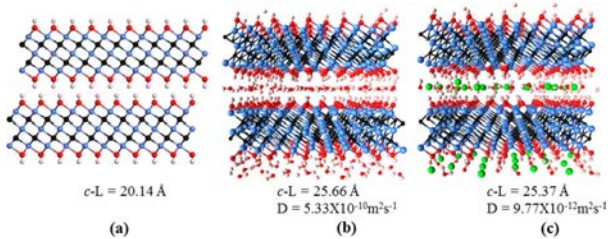


Li-migration in a carbon onion anode (Raju et al. JCTC 2015)

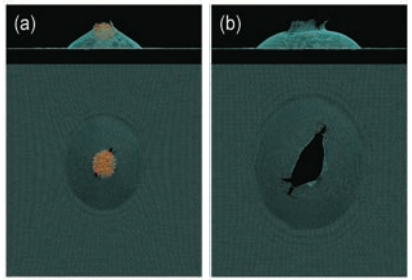
2D-materials



Stability of various MoS_2 defects (Ostadhossein et al. in progress)



Comparison of c-lattice expansion for MXenes with DFT and experiment (Osti et al. ACS-AMI 2016)

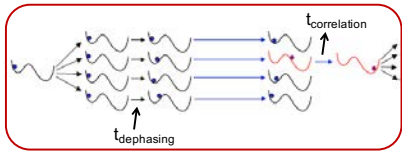


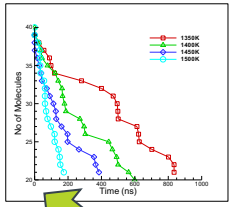
High-speed collision of a silica nanoparticle on graphene (Yoon et al, Carbon 2016)

Acceleration/meta/hyperdynamics tools connections with ReaxFF

Parallel Replica Dynamics

Joshi et al. JPC-Letters 2013





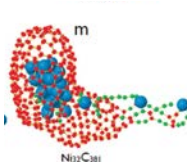
Hybrid Monte Carlo/MD

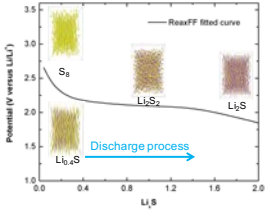
- GCMC/MD

Senftle et al. JPC-C 2014

- Force-biased MC

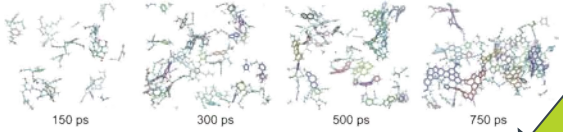
Neyts et al. ACS Nano 2010





Parallel Replica Tempering

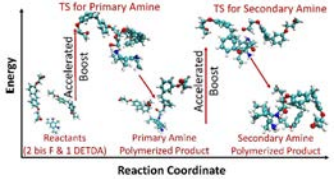
Atmani et al. Chem.Sci. 2017



ReaxFF

'Tracking' options

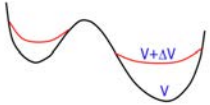
Vashisth et al. JPC-A 2018

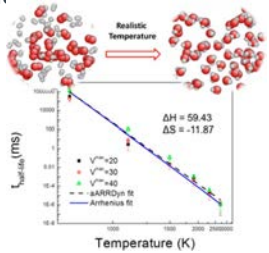


Bond boost/Collective Variable Hyperdynamics (CVHD)

Cheng et al. JACS 2014

Bal and Neyts, Chem.Sci. 2016

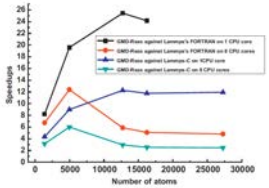




GPU accelerations

Zheng et al. J.Mol.Graph. and Mod. 2013

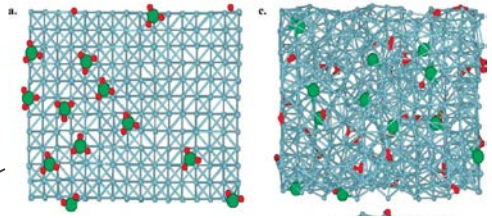
Kylasa et al. J.Comp.Phys. 2014



- Enables access to microsecond timescales
- ReaxFF at non-reactive FF speeds

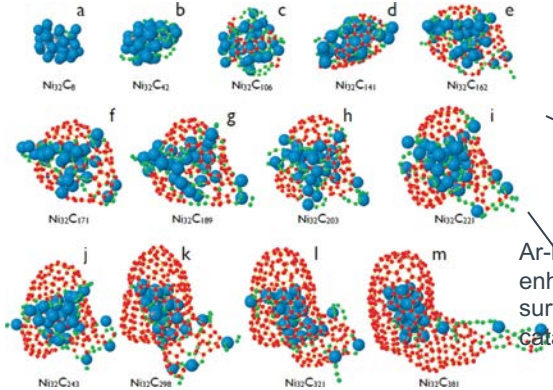
Applications to catalytic carbon-growth on Ni-surfaces

Collaborations with Jonathan Mueller (Caltech, currently U.Ulm) and Erik Neyts (U. Antwerp)

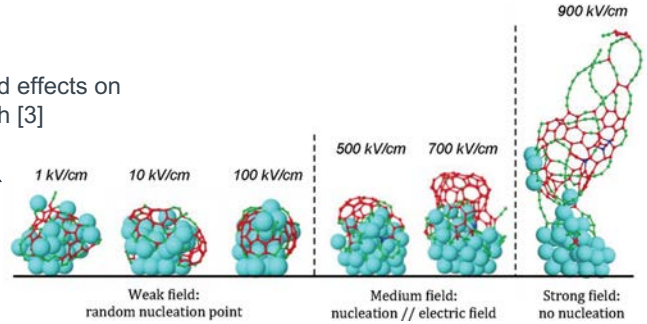


Development of Ni/hydrocarbon ReaxFF [1]

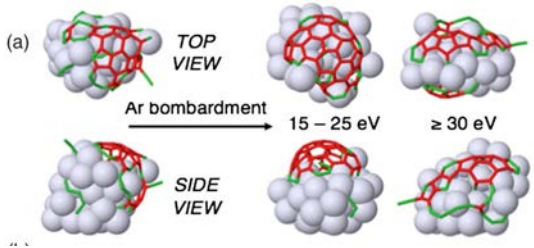
Integration of force-biased Monte Carlo [2]



Electric field effects on CNT-growth [3]



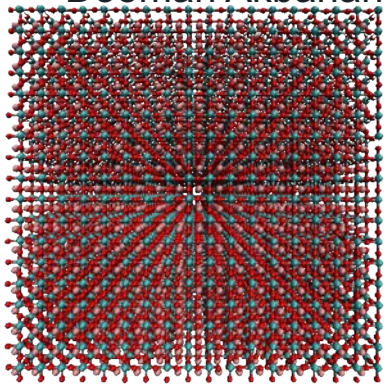
Ar-bombardment enhanced surface catalysis[4]



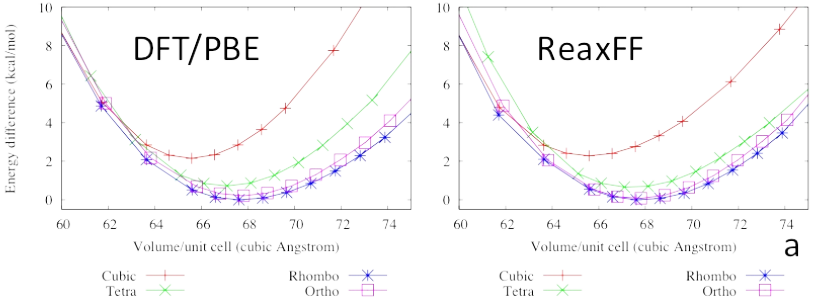
(1) Mueller, J. E.; van Duin, A. C. T.; Goddard, W. A., III. Journal of Physical Chemistry C 2010, 114, 4939.
(2) Neyts, E. C.; Shibuta, Y.; van Duin, A. C. T.; Bogaerts, A. ACS Nano 2010, 4, 6665.
(3) Neyts, E. C.; van Duin, A. C. T.; Bogaerts, A. Journal of the American Chemical Society 2012, 134, 1256.
(4) Neyts, E. C.; Ostrikov, K.; Han, Z. J.; Kumar, S.; van Duin, A. C. T.; Bogaerts, A. Physical Review Letters 2013, 110, 065501.

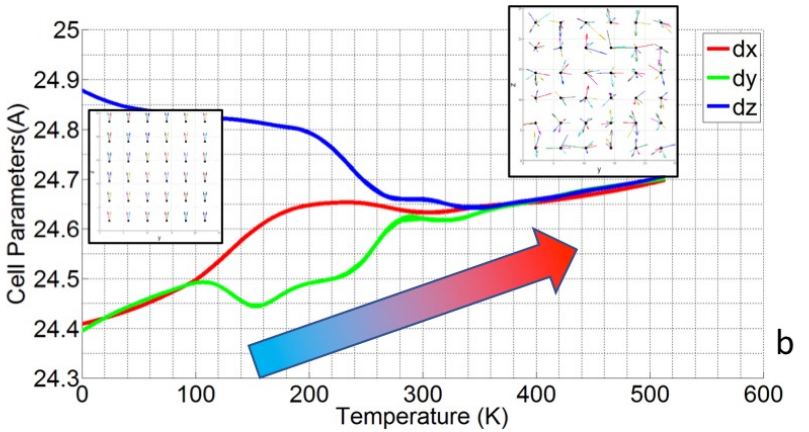
ReaxFF for solid phase ferroelectric materials [1]

Dooman Akbarian and Dundar Yilmaz



8192-atom $BaTiO_3$ supercell



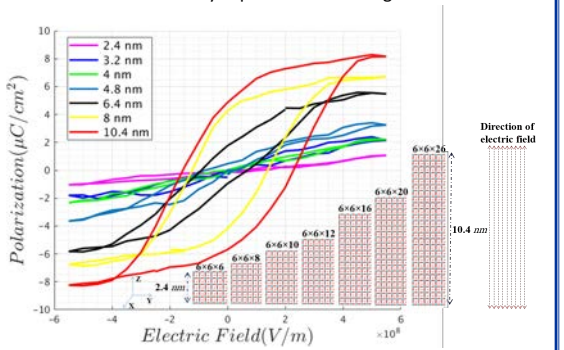


- We have successfully extended ReaxFF to $BaTiO_3$ – ReaxFF reproduces the ferroelectric to no—ferroelectric transition. This transition is reversible – including hysteresis effects
- Unmodified ReaxFF functional form → 100% transferable with other ReaxFF descriptions, enabling interface evaluation.

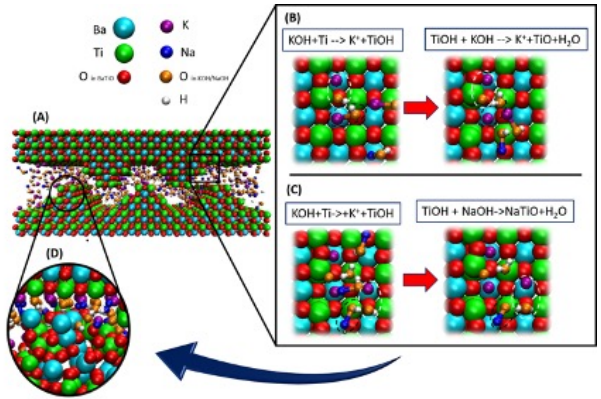
]1] Akbarian, D., Yilmaz, D., Panchapakesan, G., Dabo, I., Munro, J., van Ginhoven, R. and van Duin, A.C.T. (2019). Phys. Chem. Chem. Phys. 21, 18240-18249.

Thickness Effects

- The hysteresis loops for films thicker than 4.8 *nm* clearly show the remnant polarization, the saturation polarization, and the reversal electric field which are characteristics of a ferroelectric material.
- A minimum thickness of 4.8 *nm* is required to observe the ferroelectric hysteresis effect which is in very good agreement with the 4.4 nm value found by experimental investigations [5].



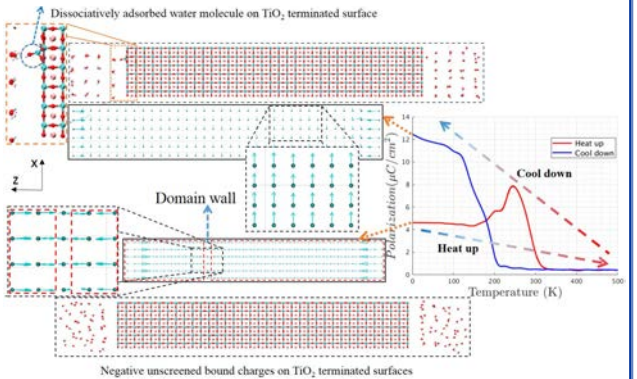
Cold sintering of $BaTiO_3$ with Na/K/OH



- Significant differences in Na/K behavior;
  K replaces Ba while Na stays in solution

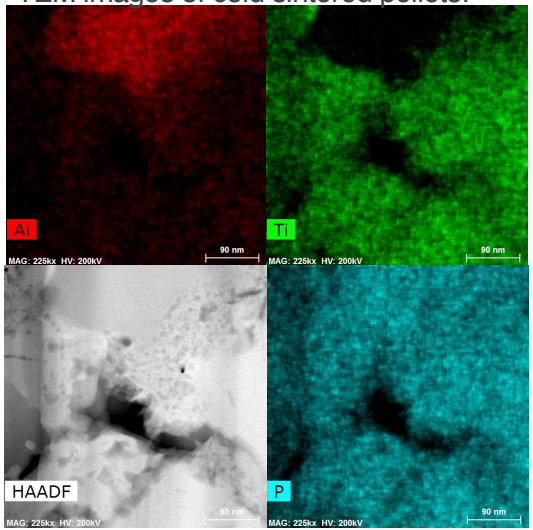
Prediction of Domain Wall Formation and Effects water on Polarization

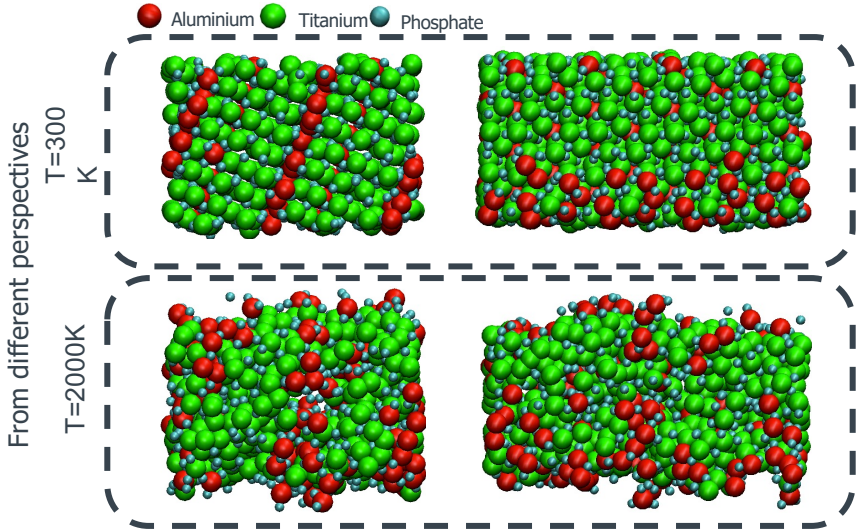
- ReaxFF can predict formation of a head-to-head 180° charged domain wall formation in a 14.4 *nm* thick $BaTiO_3$ slab with TiO_2 [0 0 1] surfaces.
- Due to TiO_2 [0 0 1] surfaces, negative unscreened bound charges exist on the surfaces of the $BaTiO_3$ slab creating a charged domain wall at the middle of the slab [6].
- When water molecules are adsorbed on the surfaces and dissociated into hydroxyl and hydrogen, the surfaces are screened by the adsorption of water molecules on the surfaces causing the polarization rearrangement in the $BaTiO_3$ slab[7].
- Adding water molecules leads to an increased amount of polarization due to the charge screening induced by adsorption of water molecules on the surfaces of $BaTiO_3$ slab[7].
- Dissociative adsorption of water molecules on the surfaces leads to a 90° domain switching confirmed by *ab-initio* study available in the literature[7].



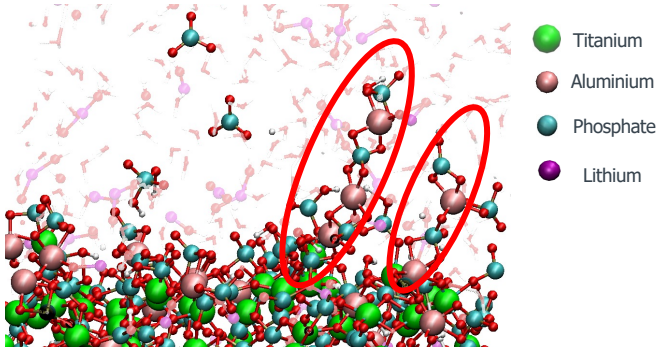
Complex oxide behavior during cold sintering - LATP

TEM images of cold sintered pellets:





- Along with the dissolution of phosphate, origination of clustering of titanium are observed, which results in aluminum and titanium rich regions. This result is in agreement with experimental TEM data.

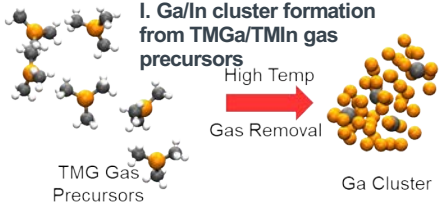


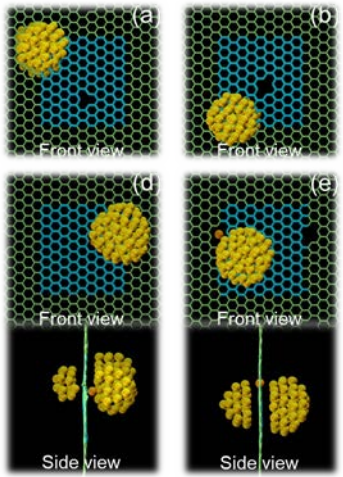
M. Y. Sengul et al. *(submitted to PCCP)*

ReaxFF Force Field Training and Development for 2D Materials' Growth and Interface Interaction Mechanisms in the Presence of Group-III Metals and Gas-Phase Precursors

Siavash Rajabpour, Qian Mao, Nadire Nayir, Joshua A Robinson, Adri C. T. Van Duin

I. Ga/In cluster formation from TMGa/TMIn gas precursors



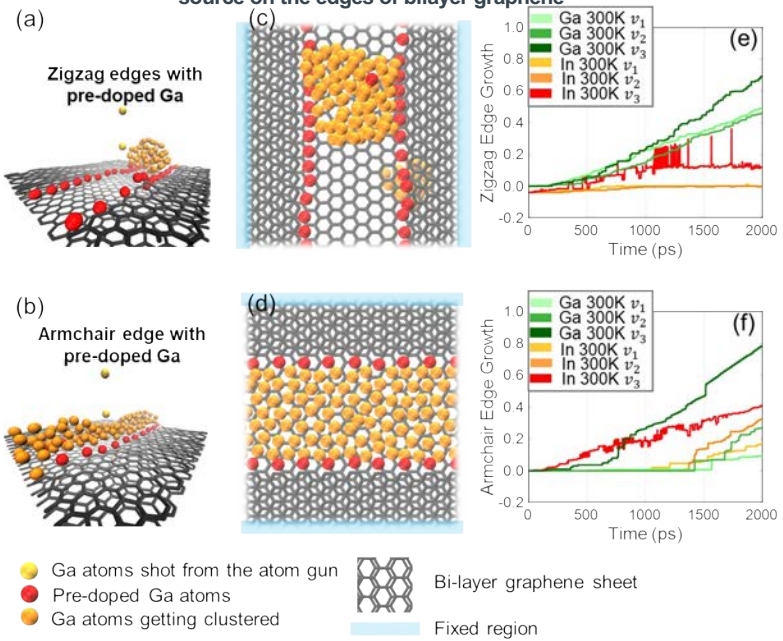


Pre-doped Ga
Non pre-doped Ga
Graphene without mapping
Graphene with PBC mapping

II. Nucleation and growth of Ga/In from an elemental metallic

Force Field Development: ReaxFF C/H/Ga and ReaxFF C/H/In force fields were developed to investigate the metal-organic chemical vapor deposition gas-phase reactions of Ga and In film growth from trimethylgallium and trimethylindium precursors.

III. Nucleation and growth of Ga/In from an elemental metallic source on the edges of bilayer graphene



Ga atoms shot from the atom gun
Pre-doped Ga atoms
Ga atoms getting clustered
Bi-layer graphene sheet
Fixed region

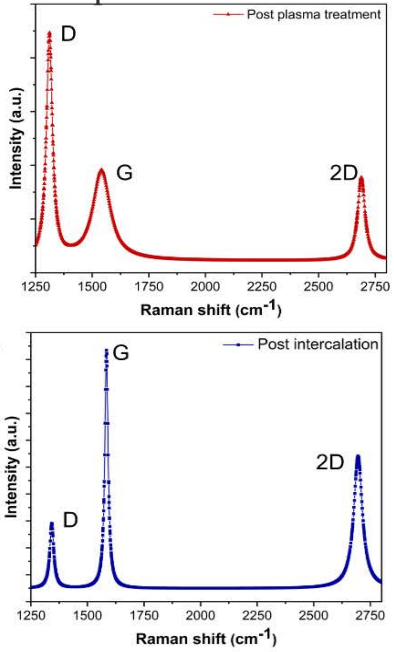
Major finding: Ga atoms growing on armchair-edged graphene not only exhibited a superior growth ratio to In atoms but also produced a widely spread 2D thin layer between graphene edges

Rajabpour, S., Mao, Q., Nayir, N., Robinson, J. A., & Van Duin, A. C. (2021). Development and Applications of ReaxFF Reactive Force Fields for Group-III Gas-Phase Precursors and Surface Reactions with Graphene in Metal–Organic Chemical Vapor Deposition Synthesis. The Journal of Physical Chemistry C, 125(19), 10747-10758.

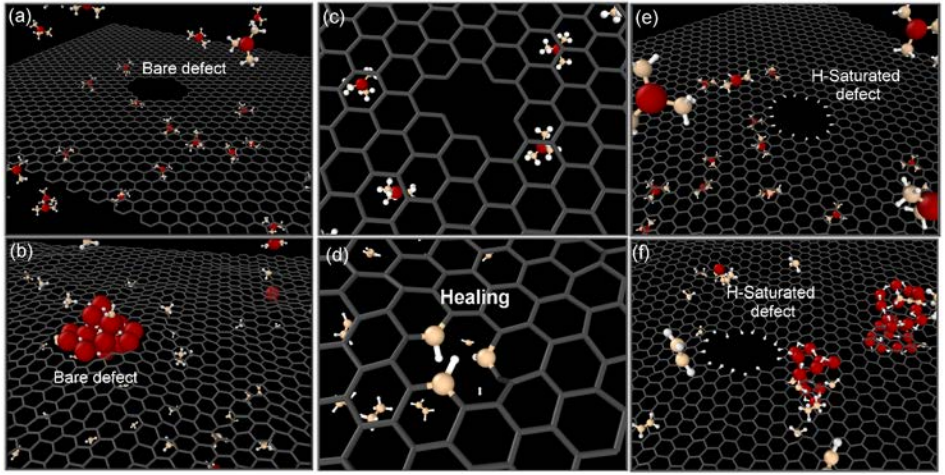
ReaxFF for 2D-Non-layered Materials (Ga, In)

ReaxFF simulations show that TMGa exposure can lead to **defect healing** by the passivation of carbon-dangling bonds by hydrocarbon and organometallic adducts, which is supported by the decreased Raman D:G ratio in Ga-intercalated graphene and by STM images.

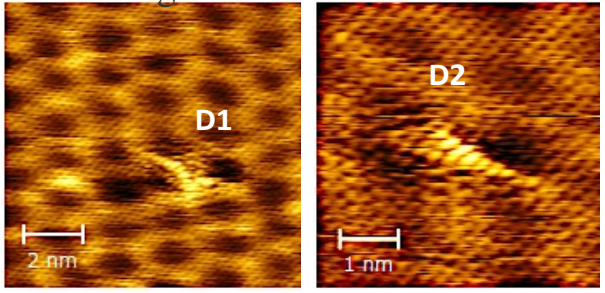
Raman spectra



ReaxFF



STM images



N. Nayir, M. Y. Sengul, A. L. Costine, P. Reinke, S. Rajabpour, A. Bansal, A. Kozhakhmetov, J. Robinson, J. M. Redwing, A. van Duin (submitted to Carbon)

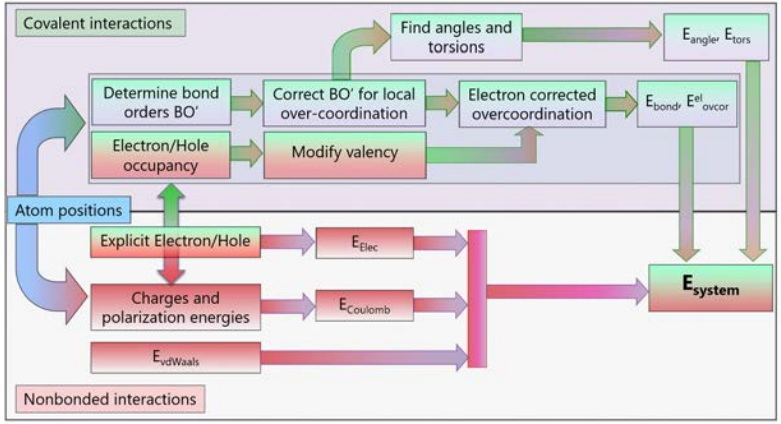
eReaxFF: concepts and background [1,2]

- Quantum Chemistry methods possess explicit electronic degrees of freedom, provide the most accurate and detailed description of chemical reactions
- However, their inherent complexity in formalism and high computational cost limit applications to relatively small length- and time-scales
- Approximate QC based methods, i.e. density functional theory (DFT) or Tight-Binding (TB) schemes have been developed as computationally advantageous alternatives to truly ab initio methods. Still, non-adiabatic dynamics using time-dependent DFT are quite expensive
- Currently, no single computational method contains the capability to simulate the coupling between electron flow and chemistry on a larger length and time scale
- Recently, explicit valence electron concept has been introduced in the electron force field (eFF) and LEWIS; they are limited in the number of elements and transferability
- Standard ReaxFF has a number of energy terms which directly accounts the effect of electron implicitly in chemical bonding, however, no explicit treatment of electron
- A detailed investigation of electron flow associated reactions or electron dynamics requires extensions to the ReaxFF concept to incorporate explicit -electron or -hole description

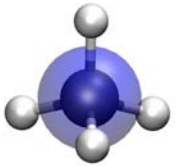
[1] Islam, M., Kolesov, G., Verstraelen, T., Kaxiras, E. and van Duin, A.C.T. (2016) eReaxFF: A Pseudo-Classical Treatment of Explicit Electrons in ReaxFF Reactive Force Field Simulations. Journal of Chemical Theory and Computation 12, 3463-3472.
[2] Leven, I., Hao, H., Tan, S., Penrod, K.A., Akbarian, D., Hossain, M.J., Evangelisti, B., Islam, M., Koski, J., Moore, S., Aktulga, H.M., van Duin, A.C.T. and Head-Gordon, T. (2021) Recent Advances for Improving the Accuracy, Transferability and Efficiency of Reactive Force Fields. Journal of Chemical Theory and Computation 17, 3237-3251.

eReaxFF: concepts and background

- Explicit electron-like and hole-like particles that carry negative (-1) and positive (+1) charges, respectively



- Electron is represented as a Gaussian function: $\psi \infty exp(-\alpha(r-r')^2)$
- Electron-nuclear electrostatic energy: $E_{nucl(i)-elec(j)} = -\frac{1}{4\pi\varepsilon_o}\beta\sum_{i,j}\frac{Z_i}{R_{ij}}erf\left(\sqrt{2\alpha}R_{ij}\right)$
- Number of electrons belongs to an atom, $n_{el}=exp(-p_{val}*R_{ij}^2)$
- Variable valency and lone electron pair
- Charge-valency coupling
- Modified over/under-coordination functional | $\Delta_i = -Val_i + \sum_{j=1}^{neighbor(i)} BO_{ij}$
- ACKS2[1] scheme is used to calculate atomic charges



<CH_4^->

ReaxFF charge calculation methods: EEM and ACKS2

Condensed form for the 'electronic energy'

$$E_{\mathrm{EEM}} = \left(\sum_A \chi_A q_A + \frac{1}{2} \eta_A q_A^2 \right) + \left(\frac{1}{2} \sum_{A,B \neq A} \frac{q_A q_B}{|\mathbf{r}_A - \mathbf{r}_B|} \right)$$

Variables: q_i Parameters: $\chi_i, \eta_i, \bar{r}_i$

Charges minimize E_{EEM} (with total charge constraint)

$$\frac{\partial E_{\mathrm{EEM}}}{\partial q_A} = \sum_A \left(\chi_A + \eta_A q_A + \sum_{B \neq A} \frac{q_B}{|\mathbf{r}_A - \mathbf{r}_B|} \right) = \chi_{\mathrm{mol}}$$

EEM equations in block matrix notation

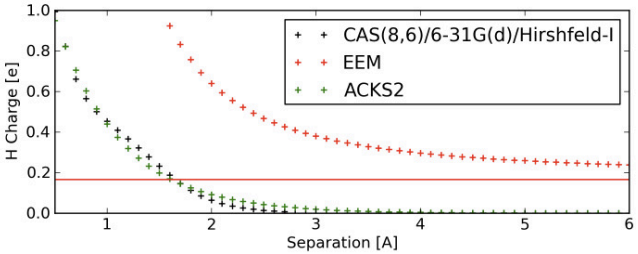
$$-\left[\begin{array}{c|c} \eta & -d \\ \hline -d^T & 0 \end{array}\right] \left[\begin{array}{c} q \\ \hline \chi_{\mathrm{mol}} \end{array}\right] = \left[\begin{array}{c} \chi \\ \hline q_{\mathrm{tot}} \end{array}\right]$$

ACKS2 equations in block matrix notation

$$-\left[\begin{array}{c|c|c|c} \eta & -d & -I & 0 \\ \hline -d^T & 0 & 0 & 0 \\ \hline -I & 0 & X_S & -d \\ \hline 0 & 0 & -d^T & 0 \end{array}\right] \left[\begin{array}{c} \Delta \\ \hline \mu_{\mathrm{mol}} \\ \hline W \\ \hline \lambda_W \end{array}\right] = \left[\begin{array}{c} \mu \\ \hline 0 \\ \hline 0 \\ \hline 0 \end{array}\right]$$

In collaboration with Toon Verstraelen (U. Gent)

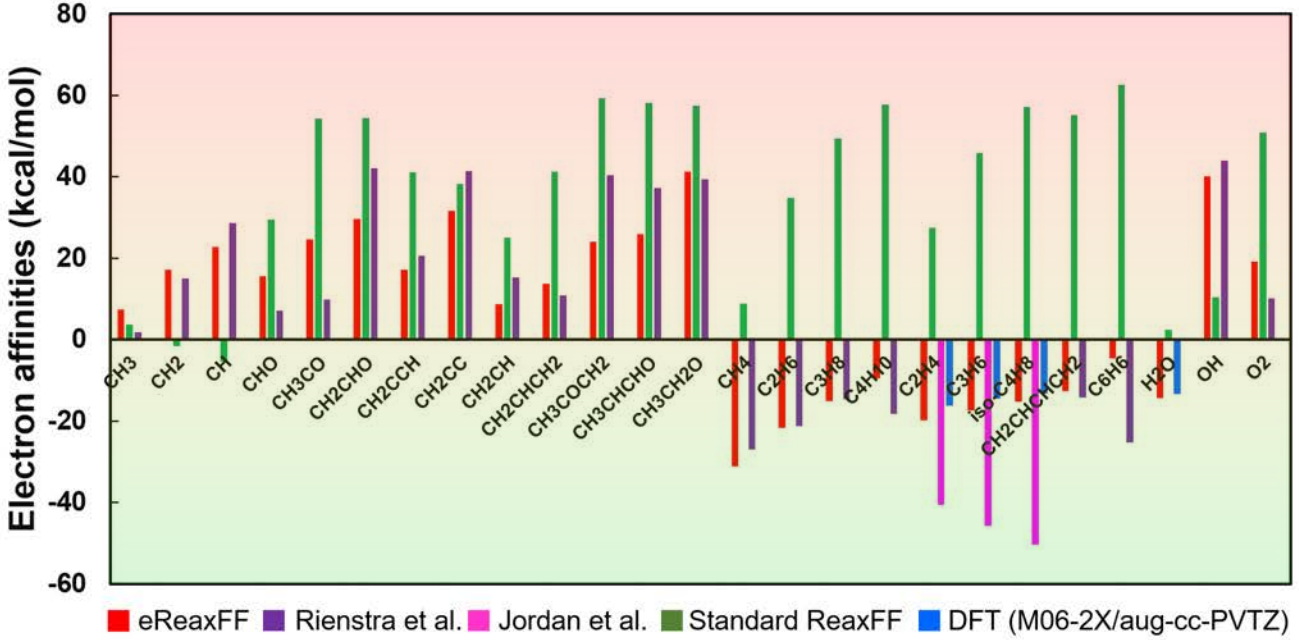
Charges on H during HF-dissociation



-EEM gives non-zero charges after bond dissociation
- ACKS2 enforces integer charges
- ACKS2 solves polarization issues (EEM: metallic)
- No need for H-bond term any more !

Verstraelen, Ayers et al. JCP 2013

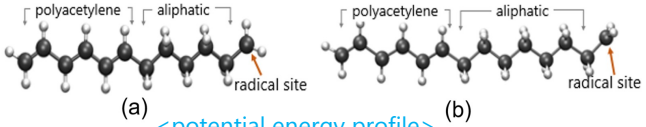
- eReaxFF force field is trained against electron affinities of various species, including saturated, unsaturated, and radical species



- eReaxFF qualitatively reproduces experimental/DFT Electron Affinities of the specie considered in the training set
- Standard ReaxFF fails to capture EAs of most of the species

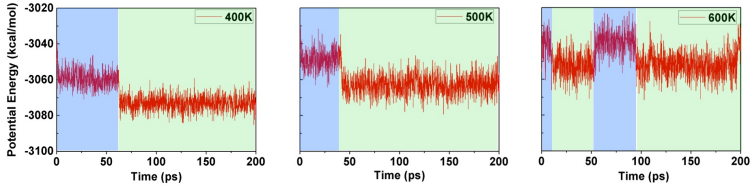
MD simulations were performed on two model hydrocarbon radicals at 400K, 500K and 600K

Mahbub Islam [1]

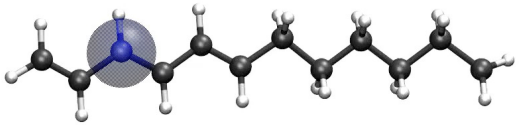


- Two radicals $C_{12}H_{19}^{\cdot}$ and $C_{14}H_{23}^{\cdot}$ are considered

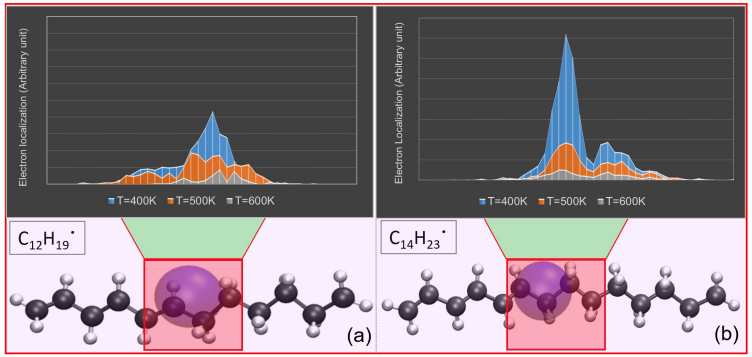
<potential energy profile>



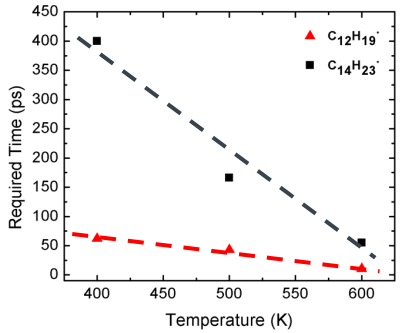
<Electron delocalization>



<Electron localization at the aliphatic and conjugate chain>



<Time-scale requirement for both radicals>

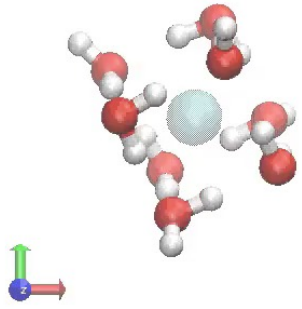


- Higher temperature accelerates electron transfer (ET) rate
- The increase in the aliphatic chain length slows down the ET
- Temperature decreases electron localization around the junction, accelerated ET at higher temperatures

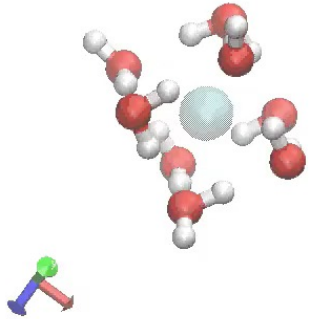
[1] Islam, M., Kolesov, G., Verstraelen, T., Kaxiras, E. and van Duin, A.C.T. (2016) eReaxFF: A Pseudo-Classical Treatment of Explicit Electrons in Improving the Accuracy, Transferability and Efficiency of Reactive Force Fields. Journal of Chemical Theory and Computation 17, 3237-3251.

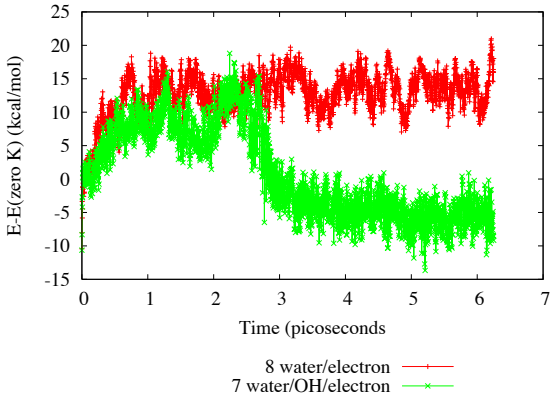
e-ReaxFF predictions for excess electron effect on water chemistry

$[H_2O]_8$ cluster with 1 excess electron



$[H_2O]_7$ cluster with 1 OH radical and 1 excess electron



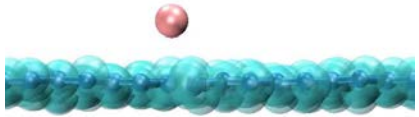


- Electron does not react with the water
- Electron is strongly stabilized by water – total binding energy 53 kcal/mol
- At t=2.5 picoseconds, OH-radical captures the electron – resulting in an exothermic formation of a OH-anion
- OH-anion/7 water system is stable
- This ReaxFF parameter set was not optimized for water - probably under-estimates water/electron interactions
- Simulation time: around 40 seconds

Development of eReaxFF force field for graphitic systems

transition to a dissociable Drude model

Jamil Hossain



- Electrons can freely move around in graphene and into the electrolyte
- The probability of electrons being grabbed by a Li^+ cation or electrolyte molecule depends on the voltage and how far the electron is from the graphene anode
- Using eReaxFF we can simulate graphene with extra electrons and see how far electrons can travel into the electrolyte before being grabbed by a Li^+ cation or electrolyte molecule
- The Hossain-2020[1] ReaxFF force field is trained in such a way that the electrolytes remain non-reactive while Li^+ is present. For electrolyte reduction Li^+ must grab an electron to become neutral Li
- In a Monte Carlo fashion few of the Li^+ cations in the electrolyte can be transformed into neutral Li and consequently electrolyte decomposition can be expected

In order to study non-zero voltage simulations of graphitic anode materials, we have developed an eReaxFF force field for carbon

Targeted qualities of the force field:

- Correct trends of electron affinities for small PAHs
- Correct equation of states for graphite in both ab-direction as well as c-direction
- In-plane diffusion of extra electron
- Restricted through-plane electron diffusion
- Behavior of extra electron diffusion in the presence of defects such as C-vacancy and sp^3 linkers
- High electron affinity for curved graphene
- Introduction of Li/Li^+ interaction with graphene at different voltages
- Li-plating on graphene

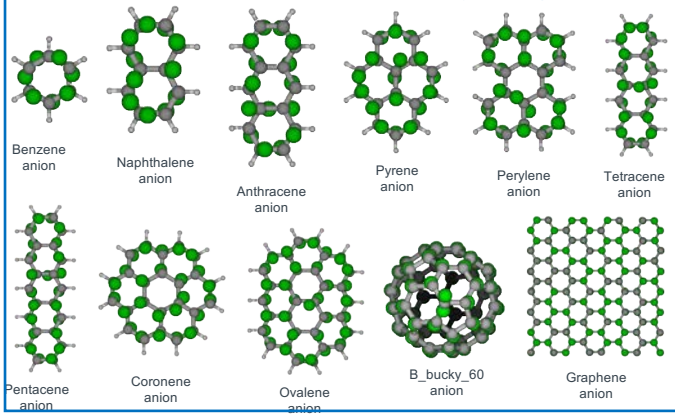
[1]Hossain, M.J., Pawar, G., Liaw, B., Gering, K.L., Dufek, E.H. and van Duin, A.C.T. (2020) Lithium-electrolyte solvation and reaction in the anode/electrolyte interface of a lithium-ion battery: A ReaxFF reactive force field study. Journal of Chemical Physics 152, 184301.

Development of eReaxFF force field for graphitic systems

transition to a dissociable Drude model

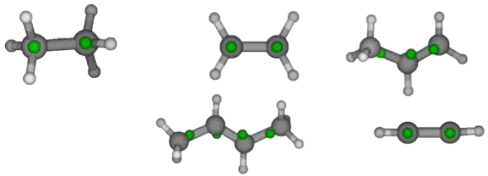
Jamil Hossain

Electron Affinities of PAH, bucky ball, graphene

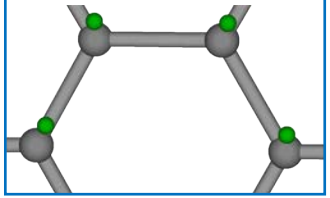


Bond dissociation energies of C-C single, double and triple bonds

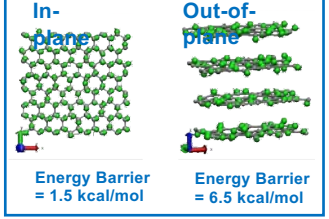
Angle bending and rotation of dihedrals of hydrocarbons



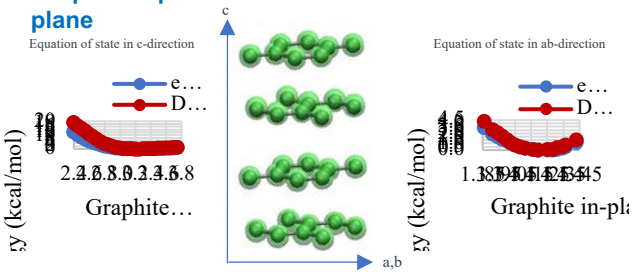
Electron orbiting the nuclei



Electron Conduction



Graphite equation of states in c direction and ab plane

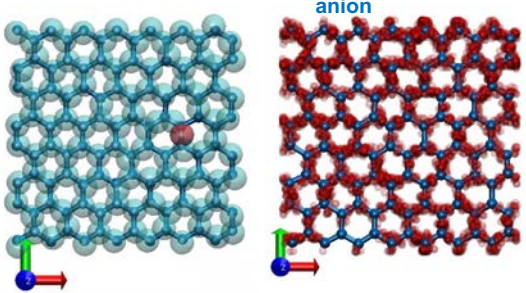


eReaxFF MD simulations

In-plane Electron Conduction

Graphene anion

Plot of the total path traveled by extra electron of graphene anion

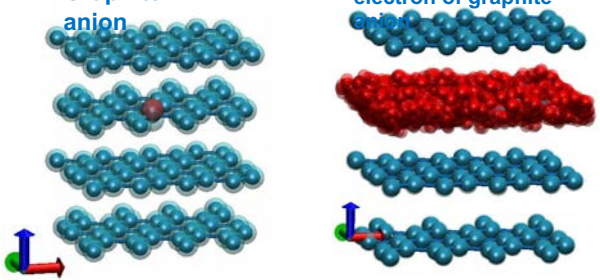


- Electron is very diffusive in the graphene plane

Out-of-plane Electron Conduction

Graphite anion

Plot of the total path traveled by extra electron of graphite anion



- At 300 K, out-of-plane electron motion is restricted
- At higher temperature and higher voltages, out-of-plane electron conduction is observed

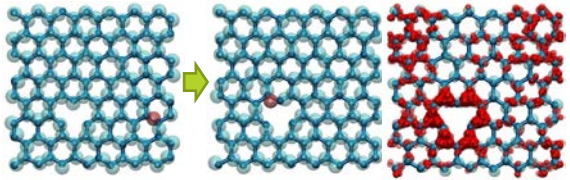
Temperature 300 K

Our eReaxFF carbon force field can

- simulate graphite as an electron conductor in the graphene plane
- simulate graphite as an electrical insulator through the graphene plane at room temperature

eReaxFF MD simulations

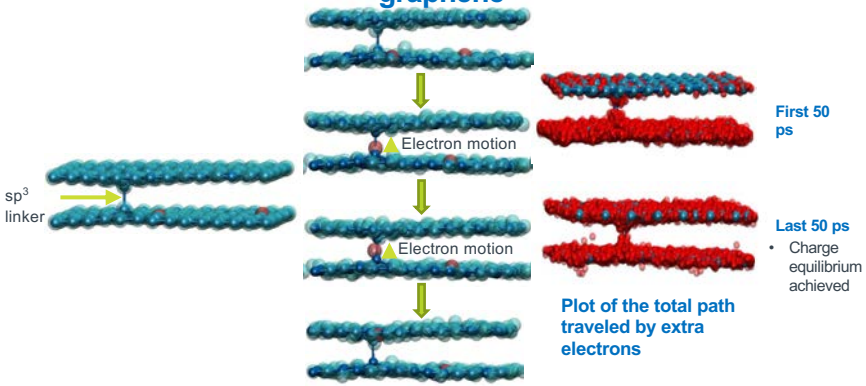
In-plane Electron Conduction in graphene anion with single C vacancy



Diffusing extra electron gets trapped at the defect site due to undercoordinated carbon atoms

Plot of the total path traveled by extra electron of graphite anion with C-vacancy

Electron Conduction in sp^3 linked bilayer graphene



First 50 ps

Last 50 ps

- Charge equilibrium achieved

Plot of the total path traveled by extra electrons

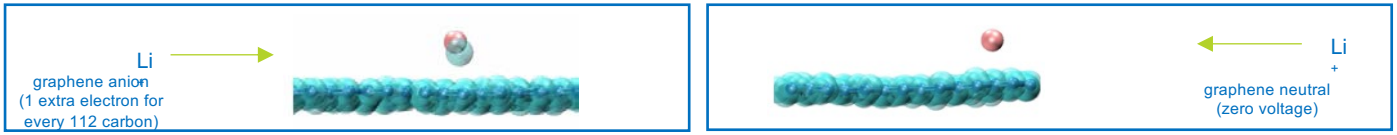
Steps involved in electron transition between layers

Temperature 300 K

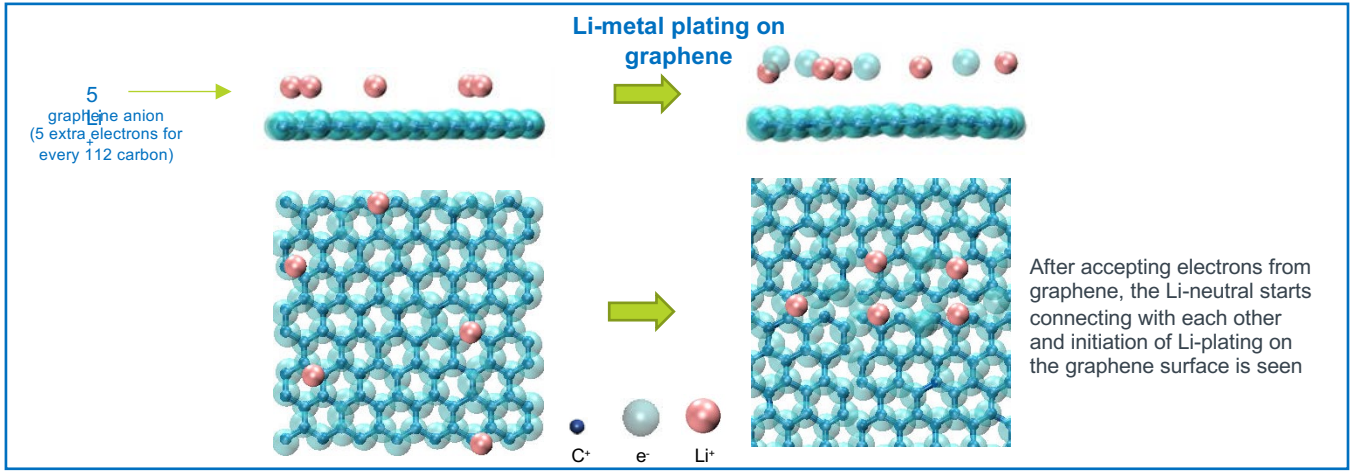
The excess electron finds its way near the sp^3 carbon of the bottom graphene layer and moves through the sp^3 linker to the top graphene layer

eReaxFF MD simulations

Li^+ cation approaching graphene anion

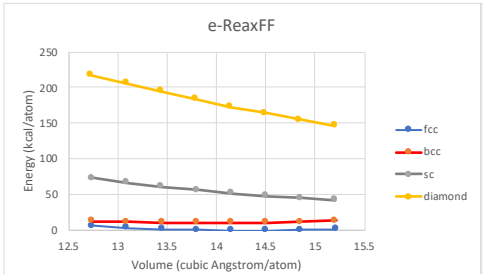


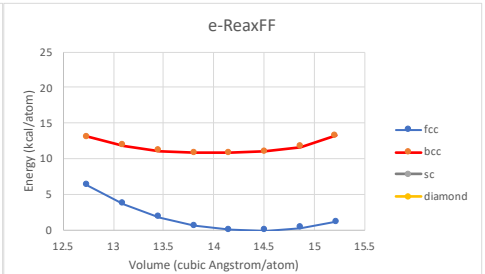
A Li^+ approaching graphene with excess charge can grab electron from graphene whereas no electron transfer is seen at the zero voltage graphene

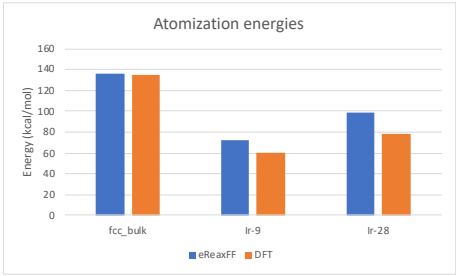


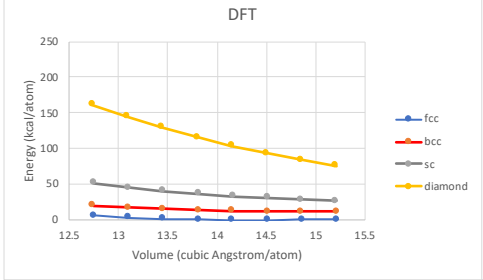
Temperature 300 K

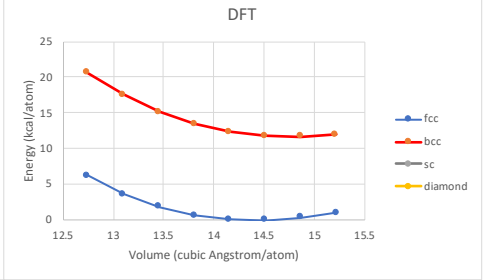
e-ReaxFF development for Ir-metal

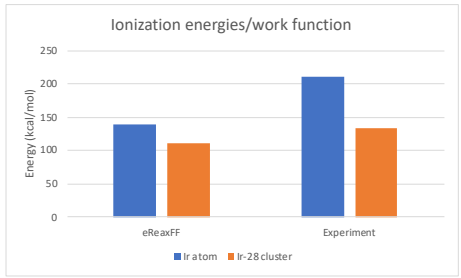








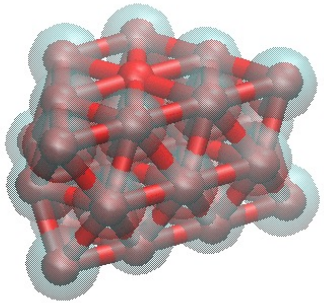


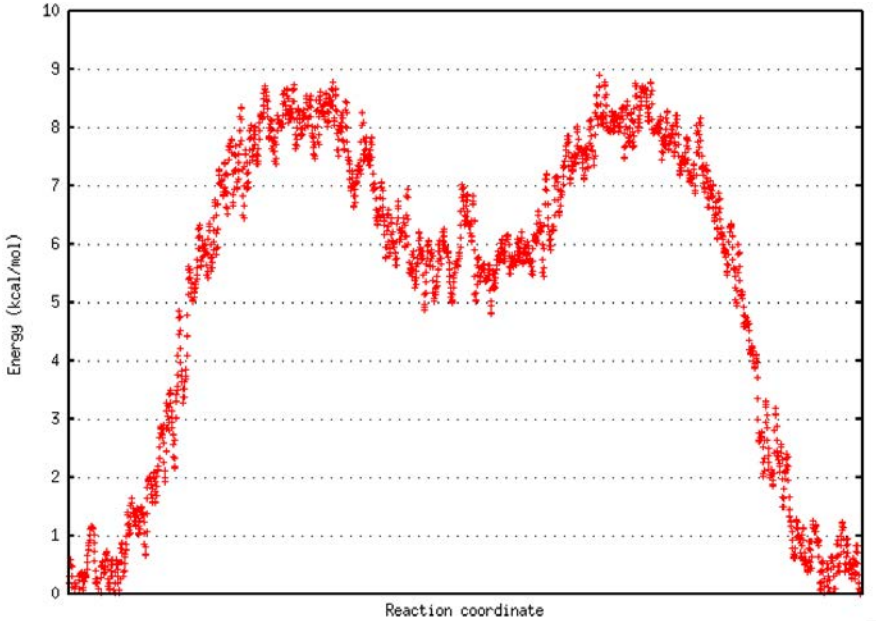


- Good reproduction of fcc equation of state and experimental ionization/work function trends

e-ReaxFF simulation on electron transfer in a Ir_{28}^{+} cluster

MD/NVT simulation at T=25K with external Gaussian restraint to drive electron.
All Ir-atoms are represented by Os^{+}/El^{-} pairs



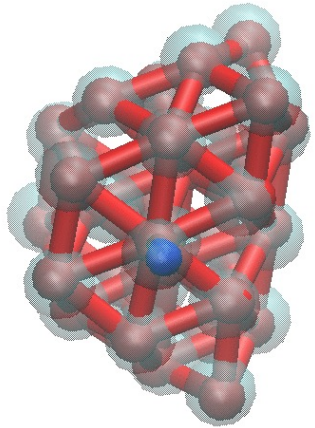


- Low barrier for electron transport
- e-ReaxFF prefers for the El-vacancy to be at a higher coordinated site
- Energy for electron removal (work function, $E(Ir_{28})-E(Ir_{28}^{+})$): 110 kcal/mol

e-ReaxFF simulation on a N-atom adsorbed on a Ir_{28} cluster

MD/NVT simulation at T=1000K.
All Ir-atoms are represented by Os^{+}/El^{-} pairs. N is blue

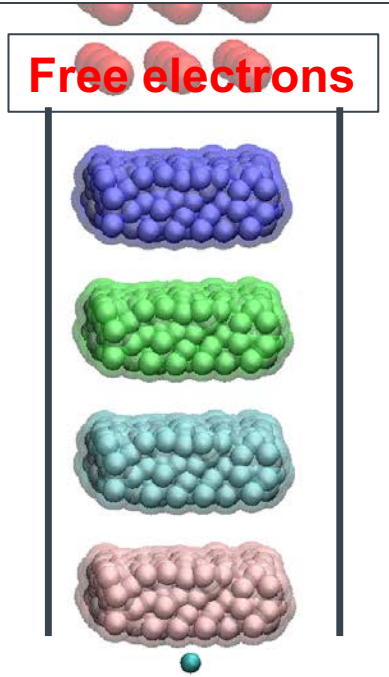
29 atoms, 29 electrons
10,000 step MD simulation, CPU time 18 seconds (MacOS-X laptop)



e-ReaxFF simulations on metal slab capacitance [1]

Ben Evangelisti

4 2D-silver slabs
(Ag^+/El^- pairs)



- Each Ag-slab adsorbs around 30 excess electrons before becoming an electron transmitting
- Enables large-scale (>> 10,000 atoms/electrons) simulation of complex charge/discharge events
- Simulation time: around 1 day on 20 cores
- This is a simulation capability looking for an application!

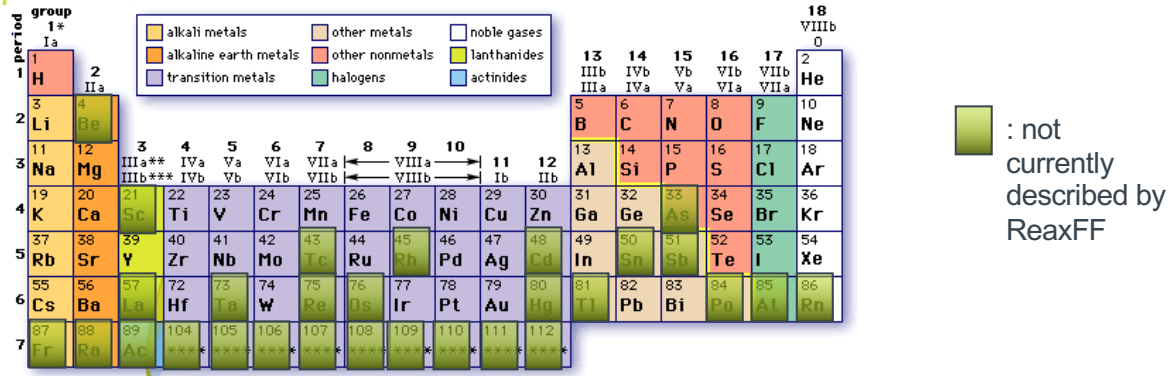
[1] Evangelisti, B., Fichthorn, K.A. and van Duin, A.C.T. (2020) An eReaxFF description of Ag nanoclusters. Journal of Chemical Physics 153, 104106.

Summary

- ReaxFF has proven to be transferable to a wide range of materials and can handle both complex chemistry and chemical diversity. Specifically, ReaxFF can describe covalent, metallic and ionic materials and interactions between these material types.

- The low computational cost of ReaxFF (compared to QM) makes the method suitable for simulating reaction dynamics for large (>> 1000 atoms) systems (single processor). ReaxFF has now been parallelized, allowing reactive simulations on >>1000,000 atoms.

- e-ReaxFF allows simulations involving electron transfer between carbon/catalyst surfaces and substrate. Expansions to ferroelectric oxides may lead to more accurate local dipole calculation and associated ferroelectric transitions



materials design

Acknowledgments

Funding:

- NSF
- DoE/NETL UCFER
- AFOSR/MURI
- AFOSR
- DoE/EFRC FIRST and MUSE centers
- Industrial sponsors (Exxon, Imerys, Western Digital, Dow, Solvay)
- British Royal Society (initial ReaxFF funding)

More information:

Websites: http://www.engr.psu.edu/adri

Office: 240 Research East
Phone: 814-863-6277
E-mail: acv13@psu.edu,

PennState

materials design

Question and Answer Session

Prof. van Duin

Pennsylvania State University and
RxFF Consulting

Dr. Ray Shan

Materials Design

Questions about Materials Design Webinars

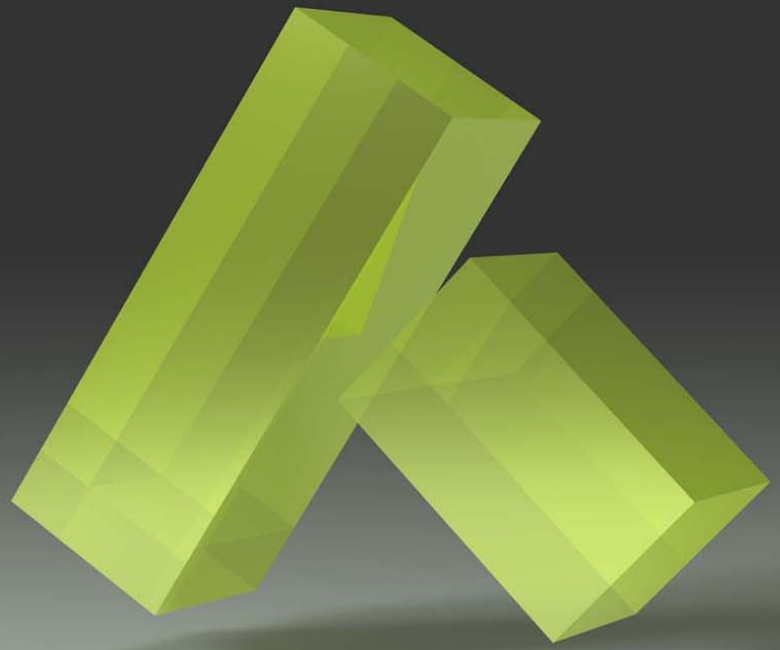
Katherine Hollingsworth

khollingsworth@materialsdesign.com

materials design

info@materialsdesign.com

www.materialsdesign.com



MedeA

Innovation by Simulation